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VEGETABLE OIL-BASED COATING AND METHOD FOR APPLICATION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to the following applications: 1) U.S. Patent Application Serial No. 09/646,356, entitled IMPROVED CELLULAR PLASTIC MATERIAL, by Thomas M. Kurth, filed September 14, 2000, which is a continuation-in-part of U.S. Patent No. 6,180,686, entitled IMPROVED CELLULAR PLASTIC MATERIAL; 2) U.S. Patent Application Serial No. 09/944,212, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE MATERIAL PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on August 31, 2001, which claims priority to U.S. Provisional Patent Application Serial No. 60/230,463, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on September 6, 2000, U.S. Provisional Patent Application Serial No. 60/239,161, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on October 10, 2000, and U.S. Provisional Patent Application Serial No. 60/251,068, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on December 4, 2000; 3) U.S. Patent Application Serial No. 09/974,301, entitled METHOD OF PRODUCING BIO-BASED CARPET MATERIAL, by Thomas M. Kurth et al., filed on October 10, 2001, which claims priority to U.S. Provisional Patent Application Serial No. 60/239,161, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on October 10, 2000, and U.S. Provisional Patent Application Serial No. 60/251,068, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on December 4, 2000; 4) U.S. Patent Application Serial No. 09/974,303, entitled OXYLATED VEGETABLE-BASED POLYOL HAVING

INCREASED FUNCTIONALITY AND URETHANE MATERIAL FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on October 10, 2001; and 5) U.S. Provisional Application Serial No. 60/251,068, entitled TRANSESTERIFIED POLYOL HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE PRODUCTS FORMED USING THE POLYOL, by Thomas M. Kurth et al., filed on December 4, 2000.

BACKGROUND OF THE INVENTION

Because of their widely ranging mechanical properties and their ability to be relatively easily machined and formed, plastic foams and elastomers have found wide use in a multitude of industrial and consumer applications. In particular, urethane materials, such as foams and elastomers, have been found to be well suited for many applications. Vehicles, for instance, contain a number of components, such as cabin interior parts or cargo lay areas, that are comprised of urethane foams and elastomers. Urethane foams are also used as carpet backing. Such urethane foams are typically categorized as flexible, semi-rigid, or rigid foams with flexible foams generally being softer, less dense, more pliable, and more subject to structural rebound subsequent to loading than rigid foams.

The production of urethane foams and elastomers are well known in the art. Urethanes are formed when isocyanate (NCO) groups react with hydroxyl (OH) groups. The most common method of urethane production is via the reaction of a polyol and an isocyanate, which forms the backbone urethane group. A cross-linking agent and/or chain extender may also be added. Depending on the desired qualities of the final urethane product, the precise formulation may be varied. Variables in the formulation include the type and amounts of each of the reactants and additives.

In the case of a urethane foam, a blowing agent is added to cause gas or vapor to be evolved during the reaction. The blowing agent is one element that assists in creating the size of the void cells in the final foam, and commonly is a solvent with a relatively low boiling point or water. A low boiling solvent evaporates as heat is produced during the exothermic isocyanate/polyol reaction to form vapor bubbles. If water is used as a blowing agent, a reaction occurs between the water and the isocyanate group to form an amine and carbon dioxide (CO_2) gas in the form of bubbles. In either case, as the reaction proceeds and the material solidifies, the vapor or gas bubbles are locked into place to form void cells. Final

urethane foam density and rigidity may be controlled by varying the amount or type of blowing agent used.

A cross-linking agent is often used to promote chemical cross-linking to result in a structured final urethane product. The particular type and amount of cross-linking agent used will determine final urethane properties such as elongation, tensile strength, tightness of cell structure, tear resistance, and hardness. Generally, the degree of cross-linking that occurs correlates to the flexibility of the final foam product. Relatively low molecular weight compounds with greater than single functionality are found to be useful as cross-linking agents.

Catalysts may also be added to control reaction times and to effect final product qualities. The catalysts generally effect the speed of the reaction. In this respect, the catalyst interplays with the blowing agent to effect the final product density. Preferably, for foam urethane production, the reaction should proceed at a rate such that maximum gas or vapor evolution coincides with the hardening of the reaction mass. The catalyst may also effect the timing or speed of curing so that a urethane foam may be produced in a matter of minutes instead of hours.

Polyols currently used in the production of urethanes are petrochemicals being generally derived from propylene or ethylene oxides. Polyester polyols and polyether polyols are the most common polyols used in urethane production. For flexible foams, polyester or polyether polyols with molecular weights greater than 2,500, are generally used. For semi-rigid foams, polyester or polyether polyols with molecular weights of 2,000 to 6,000 are generally used, while for rigid foams, shorter chain polyols with molecular weights of 200 to 4,000 are generally used. There is a very wide variety of polyester and polyether polyols available for use, with particular polyols being used to engineer and produce a particular urethane elastomer or foam having desired particular final toughness, durability, density, flexibility, compression set ratios and modulus, and hardness qualities. Generally, higher molecular weight polyols and lower functionality polyols tend to produce more flexible foams than do lower molecular weight polyols and higher functionality polyols. In order to eliminate the need to produce, store, and use different polyols, it would be advantageous to have a single, versatile, renewable component that was capable of being used to create final urethane foams of widely varying qualities.

Currently, one method employed to increase the reactivity of petroleum based polyols includes propoxylation or ethoxylation. When propoxylation or ethoxylation is done on

conventional petroleum based polyols, current industry practice is to employ about 70% propylene oxide by weight of the total weight of the polyol and propylene oxide is required to complete the reaction. Due to the large amount of alkyloxide typically used, the reaction of the alkyloxide and the petroleum based polyol is extremely exothermic and alkyloxides can be very expensive to use, especially in such high volumes. The exothermic nature of the reaction requires numerous safety precautions be undertaken when the process is conducted on an industrial scale.

Use of petrochemicals such as, polyester or polyether polyols is disadvantageous for a variety of reasons. As petrochemicals are ultimately derived from petroleum, they are a non-renewable resource. The production of a polyol requires a great deal of energy, as oil must be drilled, extracted from the ground, transported to refineries, refined, and otherwise processed to yield the polyol. These required efforts add to the cost of polyols and to the disadvantageous environmental effects of its production. Also, the price of polyols tends to be somewhat unpredictable. Their price tends to fluctuate based on the fluctuating price of petroleum.

Also, as the consuming public becomes more aware of environmental issues, there are distinct marketing disadvantages to petrochemical based products. Consumer demand for "greener" products continues to grow. The term "bio-based" or "greener" polyols for the purpose of this application is meant to be broadly interpreted to mean all polyols not derived exclusively from non-renewable resources. Petroleum and bio-based copolymers are also encompassed by the term "bio-based". As a result, it would be most advantageous to replace polyester or polyether polyols, as used in the production of urethane elastomers and foams, with more versatile, renewable, less costly, and more environmentally friendly components.

The difficulties in the past that occurred due to the use of vegetable oil as the polyols to produce a urethane product include the inability to regulate the functionality of the polyol resulting in variations in urethane product where the industry demands relatively strict specifications be met and the fact that urethane products, in the past, outperformed vegetable oil based products in quality tests, such as carpet backing pull tests.

An unresolved need therefore exists for an improved functionality, vegetable oil based polyol of increased and selectable functionality for use in manufacturing urethane materials such as, elastomers and foams. Also needed is a method of producing such urethane materials, in particular, carpet materials using the improved functionality, vegetable oil based polyol based on

a reaction between isocyanates alone or as a prepolymer, in combination with the improved functionality polyol or a blend of the improved functionality polyol and other polyols including petrochemical based polyols. The products and methods of the present invention are particularly desirable because they relate to relatively inexpensive, versatile, renewable, environmentally friendly materials such as, vegetable oil, blown soy oil, or transesterified vegetable oil that forms a polyol of increased and selectable functionality that can be a replacement for soy or petroleum based polyether or polyester polyols typically employed.

SUMMARY OF THE INVENTION

One aspect of the present invention includes a method of coating a substrate with a material by providing a substrate, an A-side reactant comprising an isocyanate, and a B-side reactant having an esterified polyol and a catalyst wherein the esterified polyol includes the reaction product of a first polyol and a vegetable oil and the first polyol comprises the reaction product of a first multifunctional compound and a second multifunctional compound, directing the A-side and B-side reactants toward the substrate, and applying the A-side and B-side reactants to the substrate to form a urethane material that contacts the substrate.

Another embodiment of the present invention includes a method of coating a substrate with a material by providing a substrate; an applicator having an A-side intake, an A-side outlet, a B-side intake, a B-side outlet, and a nozzle head; an A-side reactant including an isocyanate; and a B-side reactant where the B-side reactant includes a vegetable oil, a cross-linking agent having a multifunctional alcohol, and a catalyst, and passing the A-side reactant through the A-side intake of the applicator and the B-side reactant through the B-side intake of the applicator such that the A-side and the B-side reactants pass through the applicator nozzle head and contact the substrate to form a urethane coating.

Yet another embodiment of the present invention includes a boat hull composite having a boat hull and a urethane material where the urethane material includes the reaction product of an A-side including an isocyanate and a B-side including an esterified polyol and a catalyst where the esterified polyol includes the reaction product of a first polyol and a vegetable oil and the first polyol includes the reaction product of a first multifunctional compound and a second multifunctional compound and where the urethane material at least partially covers the boat hull.

Still another embodiment of the present invention includes a boat hull composite including a boat hull, a urethane material at least partially covering the boat hull where the urethane material includes an isocyanate and a B-side reactant wherein the B-side includes a vegetable oil, a cross-linking agent, and a catalyst.

In another embodiment of the present invention, a building material composite includes a building substrate at least partially combined with a urethane material where the urethane material includes the reaction product of an A-side having an isocyanate and a B-side having an esterified polyol and a catalyst, where the esterified polyol includes the reaction product of a first polyol and a vegetable oil and the first polyol includes the reaction product of a first multifunctional compound and a second multifunctional compound.

In yet another embodiment of the present invention, a building material includes a building substrate at least partially combined with a urethane material where the urethane material includes the reaction product of an A-side having an isocyanate and a B-side where the B-side has a vegetable oil, a cross-linking agent, and a catalyst.

Still another embodiment of the present invention includes a method of manufacturing a carpet material by providing a carpet substrate, an applicator having an A-side intake, a B-side intake, and at least one nozzle head, an A-side having an isocyanate, and a B-side having an esterified polyol and a catalyst where the esterified polyol includes the reaction product of a first polyol and a vegetable oil and the first polyol includes the reaction product of a first multifunctional compound and a second multifunctional compound.

In yet another embodiment of the present invention, a method of coating a substrate with a material includes: providing a substrate; a spray applicator having an A-side inlet, a B-side inlet, and a sprayer head including an A-side outlet and a B-side outlet; an A-side reactant having an isocyanate; and a B-side reactant having an esterified polyol, a petroleum based polyol, and a catalyst where the esterified polyol includes the reaction product of a first polyol and a vegetable oil, the first polyol includes the reaction product of a first multifunctional compound and a second multifunctional compound, directing the spray applicator toward the substrate, passing the A-side reactant through the A-side intake of the applicator and the B-side reactant through the B-side intake of the applicator, and passing the A-side reactant and the B-side reactant through the sprayer head such that the A-side and B-side reactants react and contact the substrate material.

In yet another embodiment of the present invention, a method of coating a substrate with a material includes providing a substrate; a spray applicator having an A-side inlet, a B-side inlet, and a sprayer head including an A-side outlet and a B-side outlet; an A-side reactant having an isocyanate; and a B-side reactant having a vegetable oil, a petroleum based polyol, a cross-linker, and a catalyst, directing the spray applicator toward the substrate, passing the A-side reactant through the A-side intake of the applicator and the B-side reactant through the B-side intake of the applicator, and passing the A-side reactant and the B-side reactant through the sprayer head such that the A-side and B-side reactants react and contact the substrate material.

In still another embodiment of the present invention, a vehicle component liner composite includes a vehicle component and a urethane material where the urethane material includes the reaction product of an A-side having an isocyanate and a B-side having an esterified polyol and a catalyst where the esterified polyol includes the reaction product of a first polyol and a vegetable oil and the first polyol includes the reaction product of a first multifunctional compound and a second multifunctional compound and where the urethane material at least partially covers the boat hull.

In another embodiment of the present invention, a vehicle component liner composite includes a vehicle component and a urethane material at least partially covering the boat hull where the urethane material includes an A-side having an isocyanate and a B-side wherein the B-side includes a vegetable oil, a cross-linking agent, and a catalyst.

These and other features, advantages and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an enlarged elevated view of an applicator of one embodiment of the present invention;

Fig. 2 is a section of an interior of a boat hull, which is shown having a urethane material applied thereto in accordance with an embodiment of the present invention;

Fig. 3 shows the interior of a vehicle cargo area having a urethane material applied thereto in accordance with an embodiment of the present invention;

Fig. 4 show the exterior roof portion of a building material having a urethane material applied thereto in accordance with an embodiment of the present invention;

Fig. 5 is a second of housing material, which is shown having a urethane material applied thereto in accordance with the present invention;

Fig. 6 shows a carpet material having a urethane material applied thereto in accordance with an embodiment of the present invention; and

Fig. 7 shows a carpet material having a urethane material applied thereto in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

New methods to apply to a vegetable oil based urethane material to any substrate and composition made in accordance with the methods have been developed. The vegetable oil based urethane material may comprise the vegetable oil based material produced according to the teachings of U.S. Patent No. 6,180,686 and WO 00/15684, the disclosures of which are hereby incorporated by reference. These two patent publications teach a bio-based urethane material that is the reaction product of an A-side and a B-side where the A-side includes any isocyanate, preferably a diisocyanate, (a triisocyanate or other suitable isocyanates can be used in any A-side formulation when desirable) and the B-side includes a cross-linker, preferably a multi-functional alcohol, a vegetable oil, preferably a blown vegetable oil, and a catalyst.

The vegetable oil based urethane material may also be produced from a transesterified vegetable oil based polyol, which includes the reaction product of a multifunctional alcohol and a multifunctional component, subsequently reacted with a vegetable oil. The transesterified polyol is preferably produced using a two-stage process. In the first step in the two-stage transesterification process, glycerin, a suitable multifunctional alcohol, or other suitable multifunctional compound is preferably heated to about 230 °F, and advantageously also stirred; however, a catalyst may be used instead of or in addition to heat. Next, a multifunctional component having at least two hydroxyl groups, preferably including a saccharide compound, typically a monosaccharide, disaccharide, a polysaccharide, sugar alcohol, cane sugar, honey, or mixture thereof, is slowly introduced into the glycerin until saturated. Currently, the preferred saccharide components are fructose and cane sugar. Cane sugar provides greater tensile strength and fructose provides greater elongation of the carbon chain of the polyol. Preferably, 2 parts

of the saccharide compound is added to 1 part of the multifunctional alcohol, by weight. Glycerin is a carrier for the saccharide compound component, although it does add some functional hydroxyl groups. The saccharide component is slowly added until no additional saccharide component can be added to the glycerin solution.

It is believed that the multifunctional alcohol and the saccharide component undergo an initial transesterification to form new ester products (precursors). As such, the functionality of the new polyol is selectable. The greater the functionality of the alcohol, the greater the functionality of the final new polyol.

Next, from about 200 to 300 grams (experimental amount) of vegetable oil, preferably soy oil, and most preferably blown soy oil, is heated to at least about 180° F. However, the temperature may be any temperature from about 180° F until the oil is damaged. Blown soy oil provides superior results to regular vegetable oil; however, any vegetable oil or blown vegetable oil will work. Other vegetable oils that may be utilized in the present invention include, but should not be limited to, palm oil, safflower oil, sunflower oil, canola oil, rapeseed oil, cottonseed oil, linseed, and coconut oil. When these vegetable oils are used, they too are preferably blown. However, the vegetable oils may be crude vegetable oils or crude vegetable oils that have had the soap stock and wax compound in the crude oil removed.

Once the blown soy oil has been heated, it is slowly reacted with the heated glycerin/saccharide ester, the first transesterification reaction product. The vegetable oil and the first transesterification product undergo a second transesterification reaction that increases the functionality of the resulting polyol. Lowering the amount of the saccharide component added to the vegetable oil lowers the number of functional groups available to be cross-linked with an isocyanate group when the polyol produced using the two-stage transesterification process outlined above is used to create a urethane product. In this manner, functionality of the final polyol produced by the transesterification process of the present invention may be regulated and engineered. Therefore, more rigid urethane products are formed using a polyol produced by the present invention by using increased amounts of a saccharide component. In addition, as discussed above, the higher functionality of the multifunctional alcohol may also increase the functionality of the urethane products formed using the new polyol.

Moreover, it has been contemplated that the above described transesterification process may be performed on crude or non-blown vegetable (soy) oil prior to blowing the vegetable

(soy) oil to form a pre-transesterified vegetable (soy) oil. The pre-transesterified vegetable (soy) oil may then be blown, as known, to increase its functionality. Thereafter, the transesterification process discussed above may optionally be carried out again on the blown pre-transesterified vegetable (soy) oil.

A transesterification catalyst such as tetra-2-ethylhexyl titonate, which is marketed by DuPont® as Tyzor® TOT, may be used, instead of or in addition to heat. Also, known acids and other transesterification catalysts known to those of ordinary skill may also be used.

Also, polyols having increased functionality can not only be made by the transesterification process discussed above alone, but a further increase in functionality of the vegetable oil based polyol may also be achieved by propoxylation, butyoxylation, or ethoxylation. Applicants believe that the addition of propylene oxide (propoxylation), ethylene oxide (ethoxylation), butylene oxide, (butyloxylation), or any other known alkene oxides to a vegetable oil, a crude vegetable oil, a blown vegetable oil, the reaction product of the saccharide (multifunctional compound) and the multifunctional alcohol, or the final vegetable oil based, transesterified polyol produced according to the transesterification process discussed above will further increase the functionality of the polyol thereby formed.

Also, polyols having increased functionality can not only be made by the transesterification process discussed above alone, but a further increase in functionality of a vegetable oil based polyol may also be achieved by oxylation (propoxylation, butyoxylation, or ethoxylation). The addition of propylene oxide (propoxylation), ethylene oxide (ethoxylation), butylene oxide, (butyloxylation), or any other known alkene oxides to a vegetable oil, a crude vegetable oil, a blown vegetable oil, the reaction product of the saccharide (multifunctional compound) and the multifunctional alcohol, or the final vegetable oil based, transesterified polyol produced according to the transesterification process discussed above will further increase the functionality of the polyol thereby formed.

Applicants currently believe that bio-based oxylation substances, such as, tetrahydrofuran (TMF), tetrahydrofurfuryl, tetrahydrofurfural, and furfural derivatives as well as tetrahydrofurfuryl alcohol may be used instead of or in addition to alkyloxides in the present invention.

Moreover, Applicants believe that any substance containing an active hydrogen may be oxylated to any desired degree and subsequently transesterified. Once transesterified with the

vegetable oil, a compound whose active hydrogens were not fully oxylated may be further oxylated. Some active hydrogens include OH, SH, NH, chorohydrin, or any acid group. Compounds containing these active hydrogens, such as ethylene diamine, may be partially (because it contains more than one active hydrogen) or fully oxylated and then transesterified with the multifunctional alcohol, a crude vegetable oil, a blown vegetable oil, the reaction product of the saccharide (multifunctional compound) and the multifunctional alcohol, or the final vegetable oil based, transesterified polyol produced according to the transesterification process discussed above will further increase the functionality of the polyol thereby formed.

When propoxylation or like reactions are done to the vegetable oil or the transesterified polyol, an initiator/catalyst is typically employed to start and, throughout the reaction, to maintain the reaction of the propylene oxide and the vegetable oil to the transesterified polyol. The resulting reaction is an exothermic reaction. Initiators/catalysts that may be employed in the propoxylation, ethyloxylation, or butyloxylation reaction include triethylamine, trimethylamine, or other suitable amines as well as potassium hydroxide or other suitable metal catalyst.

Significantly, while about 70% by weight of alkyloxides is typically used to fully oxylate a petroleum based polyol, when oxylation of crude, blown, or transesterified vegetable based polyols is conducted, only about 5% to about 10% of the oxylation compound is necessary. As a result, Applicants have found that, in experimental amounts, the reaction is not nearly as exothermic as a "typical" oxylation reaction using a petroleum based product. As a result, Applicants believe this will be a significant safety benefit when done at production scale. Applicants have suprisingly found that adding heat to the oxylation reaction employing a vegetable based polyol is preferred. On an industrial scale, this may provide the additional benefit of regulating reaction time. Obviously, since significantly less oxylation raw material is used when oxylation is done to the vegetable based polyol of the present invention, significant cost savings result as well. Additionally and probably most significantly, oxylation of the vegetable based polyols of the present invention, either blown or transesterified, results in a vegetable oil based polyol with improved reactive and chemical properties.

In practice, the alkyloxide or bio-based oxylation compound and a suitable catalyst/initiator are added to a vegetable oil, preferably a blown or transesterified vegetable oil and mixed. The resultant mixture is then heated until the temperature reaches about 100° C.

The temperature is held at about 100° C for about one to about two hours. The mixture is then cooled to ambient temperature while pulling a vacuum to remove any excess alkyloxide or bio-based oxylation compound.

The preparation of urethanes is well known in the art. They are generally produced by the reaction of petrochemical polyols, either polyester or polyether, with isocyanates. The flexibility or rigidity of the foam is dependent on the molecular weight and functionality of the polyol and isocyanate used.

Polyol based polyurethanes can be prepared when what is known in the art as an A-side reactant is combined with what is known in the art as a B-side reactant. The A-side reactant of the urethane of the present invention comprises an isocyanate, typically a diisocyanate such as: 4,4' diphenylmethane diisocyanate; 2,4 diphenylmethane diisocyanate; and modified diphenylmethane diisocyanate. Typically, a modified diphenylmethane diisocyanate is used. Mondur MR Light®, an aromatic polymeric isocyanate based on diphenylmethane-diisocyanate, and Mondur® MA-2903, a new generation MDI prepolymer, manufactured by Bayer® Corporation, are two specific examples of possible isocyanates that can be used. It should be understood that mixtures of different isocyanates may also be used. The particular isocyanate or isocyanate mixture used is not essential and can be selected for any given purpose or for any reason as desired by one of ordinary skill in the art.

The A-side of the reaction may also be a prepolymer isocyanate. The prepolymer isocyanate is the reaction product of an isocyanate, preferably a diisocyanate, and most preferably some form of diphenylmethane diisocyanate (MDI) and a vegetable oil. The vegetable oil can be any of the vegetables discussed previously or any other oil having a suitable number of reactive hydroxyl (OH) groups. Soy oil is particularly advantageous to use. To create the prepolymer diisocyanate, the vegetable oil, the transesterified vegetable oil or a mixture of vegetable oils and transesterified vegetable oils are mixed and allowed to react until the reaction has ended. There may be some unreacted isocyanate (NCO) groups in the prepolymer. However, the total amount of active A-side material has increased through this process. The prepolymer reaction reduces the cost of the A-side component by decreasing the amount of isocyanate required and utilizes a greater amount of inexpensive, environmentally friendly vegetable (soy) oil. Alternatively, after the A-side prepolymer is formed, additional isocyanates may be added.

The conventional petroleum-based B-side material is generally a solution of a petroleum based polyester or polyether polyol, cross-linking agent, and blowing agent. A catalyst is also generally added to the B-side to control reaction speed and effect final product qualities. As discussed *infra*, the use of a petrochemical such as, a polyester or polyether polyol is undesirable for a number of reasons.

It has been discovered that urethane materials of high quality can be prepared by substituting the petroleum based polyol in the B-side preparation with the increased and selectable functionality polyol produced by the transesterification process outlined above; or, as discussed earlier, a blown vegetable oil, a cross-linker and a catalyst; or any oxylated vegetable oil or oxylated transesterified vegetable oil as discussed herein. Using Applicants' bio-based polyols permits substantial regulation of the functionality of the resulting bio-based polyol thereby making the polyols produced by Applicants' new processes more desirable to the industry. Previously, the functionality of vegetable oil based polyols varied dramatically due to, for example, genetic or environmental reasons.

In addition to the increased and selectable functionality polyol produced by the processes outlined above, the B-side of the urethane reaction may optionally include a cross-linking agent. Surprisingly, a cross-linking agent is not required when using the new transesterified polyol to form a urethane product. Typically, a blowing agent and a catalyst are also used in the B-side of the reaction. These components are also optional, but are typically used to form urethane product, especially foams.

A currently preferred blown soy oil typically used when forming any of the bio-based polyols and urethane materials of the present invention or practicing the methods of the present invention has the following composition; however, the amounts of each component vary over a wide range. These values are not all inclusive. Amounts of each components of the oil vary due to weather conditions, type of seed, soil quality and various other environmental conditions:

<u>100% Pure Soybean Oil Air Oxidized</u>

Moisture	1.15 %
Free Fatty Acid	1-6 %, typically ≈ 3 %
Phosphorous	50-200 ppm
Peroxide Value	50-290 Meq/Kg
Iron	≈ 6.5 ppm (naturally occurring amount)
Hydroxyl Number	42-220 mgKOH/g

Acid Value	5-13 mgKOH/g
Sulfur	≈ 200 ppm
Tin	< .5 ppm

Blown soy oil typically contains a hydroxyl value of about 100-180 and more typically about 160, while unblown soy oil typically has a hydroxyl value of about 30-40. The infrared spectrum scans of two samples of the type of blown soy oil used in the present invention are shown in Figures 1 and 2. Blown soy oil and transesterified soy oil produced according to the present invention have been found to have a glass transition at about -137° C to about -120° C depending on the saccharide component used and whether one is used at all. The glass transition measures the first signs of molecular movement in the polymer at certain temperatures. The glass transition can be measured using a Dynamic Mechanical Thermal (DMT) analysis machine. Rheometric Scientific is one manufacturer of DMT machines useful with the present invention. Applicants specifically utilize a DMTA5 machine from Rheometric Scientific. Other vegetable oils may also be used in the present invention. Typically, these other vegetable oils, which may also be blown vegetable oils, include rapeseed oil, cottonseed oil, palm oil, safflower oil, and canola oil; however, one of ordinary skill may be aware of other suitable bio-based polyols that will function within the broad concepts of the present invention.

Except for the use of the bio-based polyol replacing the petroleum based polyol, the preferred B-side reactant used to produce urethane foam is generally known in the art. Accordingly, preferred blowing agents, which may be used for the invention, are those that are likewise known in the art and may be chosen from the group comprising 134A HCFC, a hydrochloroflurocarbon refrigerant available from Dow Chemical Co. of Midland, MI; methyl isobutyl ketone (MIBK); acetone; a hydroflurocarbon; cyclopentane; methylene chloride; any hydrocarbon; and water or mixtures thereof. Presently, a mixture of cyclopentane and water is preferred. Another possible blowing agent is ethyl lactate, which is derived from soybeans and is bio-based. At present, water is the preferred blowing agent when a blowing agent is used. The blowing agents, such as water, react with the isocyanate (NCO) groups, to produce a gaseous product. The concentrations of other reactants may be adjusted to accommodate the specific blowing agent used in the reaction.

As discussed above, when blown soy oil is used to prepare the transesterified polyol of the B-side, the chain extender (cross-linking agent) may be removed from the B-side of the

urethane reactions and similar properties to urethane products produced using soy oil according to the teachings of WO 00/15684 and U.S. Patent No. 6,180,686, the disclosures of which are hereby incorporated by reference, are achieved.

If cross-linking agents are used in the urethane products of the present invention, they are also those that are well known in the art. They must be at least di-functional (a diol). The preferred cross-linking agents for the foam of the invention are ethylene glycol; 1,4 butanediol; diethanol amines; ethanol amines; tripropylene glycol, however, other diols and triols or greater functional alcohols may be used. It has been found that a mixture of tripropylene glycol; 1,4 butanediol; and diethanol amines are particularly advantageous in the practice of the present invention. Dipropylene glycol may also be used as a cross-linking agent. Proper mixture of the cross-linking agents can create engineered urethane products of almost any desired structural characteristics.

In addition to the B-side's vegetable oil, the optional blowing agent(s), and optional cross-linking agents, one or more catalysts may be present. The preferred catalysts for the urethanes of the present invention are those that are generally known in the art and are most preferably tertiary amines chosen from the group comprising DABCO 33-LV® comprised of 33% 1,4 diaza-bicyclco-octane (triethylenediamine) and 67% dipropylene glycol, a gel catalyst available from the Air Products Corporation; DABCO® BL-22 blowing catalyst available from the Air Products Corporation; POLYCAT® 41 trimerization catalyst available from the Air Products Corporation; Dibutyltin dilaurate; Dibutyltin diacetate; stannous octane; Air Products' DBU® (1,8 Diazabicyclo [5.4.0] dibutyltin dilaurate); and Air Products' DBU® (1,8 Diazabicyclo [5.4.0] dibutyltin diacetate). Other amine catalysts, including any metal catalysts, may also be used and are known by those of ordinary skill in the art.

Also as known in the art, when forming foam urethane products, the B-side reactant may further comprise a silicone surfactant which functions to influence liquid surface tension and thereby influence the size of the bubbles formed and ultimately the size of the hardened void cells in a final urethane foam product. This can effect foam density and foam rebound (index of elasticity of foam). Also, the surfactant may function as a cell-opening agent to cause larger cells to be formed in the foam. This results in uniform foam density, increased rebound, and a softer foam.

A molecular sieve may further be present to absorb excess water from the reaction mixture. The preferred molecular sieve of the present invention is available under the trade name L-paste™.

The urethane materials (products) of the present invention are produced by combining the A-side reactant with the B-side reactant in the same manner as is generally known in the art. Advantageously, use of the polyols of the present invention to replace the petroleum based polyol does not require significant changes in the method of performing the reaction procedure. Upon combination of the A and B side reactants, an exothermic reaction ensues that may reach completion in anywhere from a few seconds (approximately 2-4) to several hours or days depending on the particular reactants and concentrations used. Typically, the reaction is carried out in a mold or allowed to free rise. The components may be combined in differing amounts to yield differing results, as will be shown in the Examples presented below.

A petroleum based polyol such as polyether polyol (i.e., Bayer corporation's Multranol® 3901 polyether polyol and Multranol® 9151 polyether polyol), polyester polyol, or polyurea polyol may be substituted for some of the transesterified polyol in the B-side of the reaction, however, this is not necessary. Polyurea polyols are especially useful to accelerate the curing time of the urethane materials of the present invention when applied suing an impingement mix spray applicator. This preferred B-side formulation is then combined with the A-side to produce a urethane material. The preferred A-side, as discussed previously, is comprised of methylenebisdiphenyl diisocyanate (MDI) or a prepolymer comprised of MDI and a vegetable oil, preferably soy oil or a prepolymer of MDI and the transesterified polyol.

Flexible urethane foams may be produced with differing final qualities by not only regulating the properties of the transesterified polyol, but by using the same transesterified polyol and varying the particular other reactants chosen. For instance, it is expected that the use of relatively high molecular weight and high functionality isocyanates will result in a less flexible foam than will use of a lower molecular weight and lower functionality isocyanate when used with the same transesterified polyol. Likewise, as discussed earlier, the higher the functionality of the polyol produced by the transesterification process, the more rigid the foam produced using it will be. Moreover, it has been contemplated that chain extenders may also be employed in the present invention. For example, butanediol, in addition to acting as a cross-linker, may act as a chain extender.

Urethane elastomers can be produced in much the same manner as urethane foams. It has been discovered that useful urethane elastomers may be prepared using the transesterified polyol to replace some of or all of the petroleum based polyester or the polyether polyol. The preferred elastomer of the invention is produced using diphenylmethane diisocyanate (MDI) and the transesterified polyol. A catalyst may be added to the reaction composition. The resulting elastomer has an approximate density of about 52 lb. to about 75 lb. per cubic foot.

Applicants have also found that soybean oil and most other vegetable oils have C_3 and C_4 acid groups, which cause bitter smells when the vegetable polyols are reacted with isocyanates. In order to remove these acid groups and the resultant odor from the end use product, Applicants have also developed a way to effectively neutralize these lowering acids with the functionality of the polyol.

Applicants blow nitrogen (N_2) through a solution of about 10% ammonium hydroxide. Nitrogen gas was selected because it does not react with the ammonium hydroxide. Any gas that does not react with the ammonium hydroxide while still mixing the ammonium hydroxide through the vegetable oil would be acceptable. The ammonium hydroxide neutralizes acid groups that naturally occur in the vegetable oil. The pH of transesterified, blown, and crude vegetable oil typically falls within the range of from about 5.9-6.2. Vegetable oil neutralized by the above-identified process has a typical pH range of from about 6.5 to about 7.2, but more typically from about 6.7 to 6.9. The removal of these C_3 and C_4 acid groups results in a substantial reduction in odor when the neutralized polyols are used to form isocyanates. For most bio-based urethane applications of the present invention, the vegetable oil is typically neutralized prior to further modification to the vegetable oil to increase or decrease its functionality. Neutralization of the vegetable oil is not required to carry out any of the methods of the present invention.

The following examples are the preparation of polyols of the present invention, as well as foams and elastomers of the invention formed using the transesterified polyol. The examples will illustrate various embodiments of the invention. The A-side material in the following examples is comprised of modified diphenylmethane diisocyanate (MDI), unless otherwise indicated; however, any isocyanate compound could be used.

Also, "cure," if used in the following examples, refers to the final, cured urethane product taken from the mold. The soy oil used in the following examples is blown soy oil. Catalysts used include "DABCO 33-LV®," comprised of 33% 1,4-diaza-bicyclo-octane and 67% dipropylene glycol available from the Air Products Urethanes Division; "DABCO® BL-22," a tertiary amine blowing catalyst also available from the Air Products Urethanes Division; "POLYCAT® 41" (n, n', n", dimethylamino-propyl-hexahydrotriazine tertiary amine) also available from the Air Products Urethanes Division; dibutyltin dilaurate (T-12); dibutyltin diacetate (T-1); and Air Products DBU® (1,8 Diazabicyclo [5.4.0]). The structures of the Air Products DBU®'s (1,8 Diazabicyclo [5.4.0]) used in the present invention are shown in Figure 4.

A blowing catalyst in the following examples effects the timing of the activation of the blowing agent. Some of the examples may include "L-paste™," which is a trade name for a molecular sieve for absorbing water. Some may also contain "DABCO® DC-5160" or "Air Products DC193®", both are silicone surfactants available from Air Products Urethane Division.

EXAMPLES

All percentages referred to in the following examples refer to weight percent, unless otherwise noted.

Example 1

Transesterification

2.5%	Glycerin
5.0%	Sorbitol
92.5%	Polyurea polyol and Blown soy oil mixture

Elastomer Formation

B-side:

97 g	Transesterified polyol formed above
	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3%	Butanediol (cross-linker)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 55 parts A-side to 100 parts B-side.

Example 2

Transesterification

2.5%	Glycerin
5.0%	Sorbitol
92.5%	Polyurea polyol and Blown soy oil

Elastomer Formation

B-side:

97%	Transesterified polyol formed above
	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3%	Dipropylene glycol (chain extender)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 46 parts A-side to 100 parts B-side.

Example 3

Transesterification

2.5%	Glycerin
5.0%	Sorbitol
92.5%	Blown soy oil

Elastomer Formation

B-side:

97%	Transesterified polyol formed above
	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3%	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side.

Example 4

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85.0%	Blown soy oil

Elastomer Formation

B-side:

97%	Transesterified polyol formed above
	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3%	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side.

Example 5

Transesterification

10.0%	Glycerin
20.0%	Sorbitol
70.0%	Blown soy oil

Elastomer Formation

B-side:

	Transesterified polyol formed above
	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side.

Example 6

Transesterification

12.0%	Glycerin
24.0%	Sorbitol

12.0%	Polyurea polyol
52.0%	Blown soy oil

Elastomer Formation

B-side: Transesterified polyol formed above
Heat (190°F) was used to catalyze the reaction
Butanediol (cross-linker)

A-side: Modified monomeric MDI (Mondur® MA-2903)

Example 7

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85%	Polyurea polyol and Blown soy oil mixture

Elastomer Formation

B-side:

40.0 g	Transesterified polyol formed above
0.3 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
10.0 g	Polyether polyol (Bayer Multranol® 9151)
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 38 parts A-side to 100 parts B-side.

Example 8

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85%	Polyurea polyol and Blown soy oil mixture

Elastomer Formation

B-side:

30.0 g	Transesterified polyol formed above
20.0 g	Polyether polyol (Bayer Multranol® 9151)

3.0 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 31 parts A-side to 100 parts B-side.

Example 9

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85.0%	Blown soy oil

Elastomer Formation

B-side:

50.0 g	Transesterified polyol formed above
0.4 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 60 parts A-side to 100 parts B-side.

Example 10

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
5.0%	Polyurea polyol
80.0%	Blown soy oil

Elastomer Formation

B-side:

40.0 g	Transesterified polyol formed above
0.4 g	Air Products DBU® = urethane catalyst

	(1,8 Diazabicyclo [5.4.0])
2.4 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 40 parts A-side to 100 parts B-side.

Example 11

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
5.0%	Polyurea polyol
80.0%	Blown soy oil

Elastomer Formation

B-side:

40.0 g	Transesterified polyol formed above
0.4 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
2.4 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 100 parts A-side to 100 parts B-side.

Example 12

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
12.0%	Polyurea polyol
73.0%	Blown soy oil

Elastomer Formation

B-side:

50.0 g	Transesterified polyol formed above
0.4 g	Air Products DBU® = urethane catalyst

	(1,8 Diazabicyclo [5.4.0])
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side and cured at a temperature of 162° F.

Example 13

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85.0%	Blown soy oil

Elastomer Formation

B-side:

50.0 g	Transesterified polyol formed above
0.4 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 80 parts A-side to 100 parts B-side and cured at a temperature of 166° F.

Example 14

Transesterification

5.0%	Glycerin
10.0%	Sorbitol
85.0%	Blown soy oil

Elastomer Formation

B-side:

50.0 g	Transesterified polyol formed above
0.4 g	Dibutyltin diacetate (T-1) - catalyst
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side and cured at a temperature of 153° F.

Example 15

Transesterification

1.0%	(6.66g) Glycerin
3.0%	(13.4g) Sorbitol
400.0 g	Blown soy oil

This mixture was heated at 196°F for 1.5 hours.

Example 16

20.0 g of Glycerin heated and stirred at 178° F
Introduced 40.0 g sorbitol slowly for about 4 minutes
Stayed milky until about 15 minute mark
At temperatures above 120° F, the solution was very fluid and clear. At temperatures under 120° F, the solution was clear; however, it was very viscous.
Added this mixture to 200.0 g of blown soy oil
200.0 g of blown soy oil heated to 178° F
Introduced sorbitol, glycerin mixture as follows:
Added 10.0 g turned very cloudy within 30 seconds. Could not see the bottom of the beaker

Still very cloudy after 5 minutes and added 10.0 g
Viscosity increased and had to reduce paddle speed after 10 minutes
Viscosity reduced somewhat after about 18 minutes
A further reduction in viscosity after about 21 minutes

This was mixed in a 500 ML beaker with a magnetic paddle. The scientists were not able to see through the beaker. After about 21 minutes, a vortex appended in the surface indicating a further reduction in viscosity. At this time, the mixture lightened by a visible amount. Maintained heat and removed.

Reacted the new polyol with Modified Monomeric MDI, NCO-19.

New Polyol	100%
DBU	0.03%
MDI	50 p to 100 p of about Polyol

Reaction:
Cream time about 30 seconds
Tack free in about 45 seconds

Good physical properties after about 2 minutes

The reaction looked good, the material showed no signs of blow and seemed to be a good elastomer. It does however exhibit some signs of too much cross-linking and did not have the amount of elongation that would be optimal.

A comparative reaction run along side with the un-modified blown soy oil was not tack free at 24 hours.

Example 17

Transesterification

1.0%	Glycerin
3.0%	Sorbitol
96.0%	Blown soy oil

Elastomer Formation

B-side:

50.0 g	Transesterified polyol formed as in Example 15
0.5 g	Dibutyltin diacetate (T1) - catalyst
3.0 g	Dipropylene glycol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side and cured at a temperature of 154° F for 4 minutes.

Example 18

B-side:

50.0 g	Transesterified polyol formed from 20g Dipropylene Glycol, 5g Glycerin, and 20g sorbitol blended with 200g blown soy oil
0.3 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side.

Example 19

Transesterification

750 g	Blown soy oil
150 g	Glycerin
75 g	Cane sugar

Example 20

B-side:

40.0 g	Transesterified polyol formed as in Example 19
10.0 g	Polyether polyol (Bayer Multranol® 9151)
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.6 g	Dibutyltin diacetate

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 57 parts A-side to 100 parts B-side and was set up on 20 seconds.

Example 21

B-side:

50.0 g	Transesterified polyol formed as in Example 19
10.0 g	Polyether polyol (Bayer Multranol® 9151)
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.6 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 71 parts A-side to 100 parts B-side.

Example 22

B-side:

40.0 g	Transesterified polyol formed as in Example 19
10.0 g	Polyether polyol (Bayer Multranol® 9151)
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.6 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 45 parts A-side to 100 parts B-side.

Example 23

B-side:

100.0 g	Transesterified polyol formed as in Example 19
20.0 g	Polyether polyol (Bayer Multranol® 9151)
3.0 g	Dipropylene Glycol
3.0 g	Butanediol
0.7 g	Dibutyltin diacetate (T1)
228.6	calcium carbonate filler

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 25 parts A-side to 100 parts B-side.

Example 24

B-side:

20.0 g	Transesterified polyol formed as in Example 19
5.0 g	Transesterification from Example 25
0.6 g	Dipropylene Glycol
0.7 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903).

The B-side was combined with the A-side in a ratio of 57 parts A-side to 100 parts B-side and was set up on 20 seconds.

Example 25

Transesterification

100 g	Blown soy oil
27 g	63% glycerin and 37% cane sugar reaction product mixture

The above was heated at a temperature of 230°F and mixed for 15 minutes.

Example 26

Transesterification

100.0 g	Blown soy oil
13.5 g	63% glycerin and 37% cane sugar reaction product mixture

The above was heated at a temperature of 220°F.

Example 27

Transesterification

400 g	Blown soy oil
12 g	33% Glycerin and 66% Sorbitol

The glycerin and sorbitol product was preheated to 195° F. The total mixture was heated for 15 minutes at 202° F.

Example 28

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
0.5 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 134° F for 4 minutes.

Example 29

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
0.8 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 67 parts A-side to 100 parts B-side.

Example 30

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
1.5 g	Water
0.8 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 90 parts A-side to 100 parts B-side.

Example 31

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
1.5 g	Water
0.8 g	Dibutyltin diacetate (T1) - catalyst
0.2 g	Silicon surfactant (Air Products® DC193)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side.

Example 32

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
1.5 g	Water
0.6 g	Dibutyltin diacetate (T1) – catalyst
0.3 g	Tertiary block amine catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 74 parts A-side to 100 parts B-side.

Example 33

B-side:

50.0 g	Transesterified polyol formed as in Example 27
3.0 g	Dipropylene glycol
1.5 g	Water
0.2 g	Silicon surfactant (Air Products® DC193)
1.1 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 55 parts A-side to 100 parts B-side.

Example 34

Transesterification:

50.0 g	Blown soy oil
6.0 g	33% Glycerin and 66% Sorbitol reaction product mixture

Example 35

B-side:

50.0 g	Transesterified polyol formed as in Example 34
3.0 g	Dipropylene glycol
0.6 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 148° F for 3 minutes.

Example 36

Transesterification

20.0 g	Glycerin
40.0 g	Brown cane sugar

The above was heated at a temperature of 250° F and mixed. 30 g of wet mass was recovered in a filter and removed.

Example 37

B-side:

50.0 g	Transesterified polyol formed as in Example 36
3.0 g	Dipropylene glycol
1.0 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 67 parts A-side to 100 parts B-side at a temperature of 171° F for one minute.

Example 38

B-side:

50.0 g	Transesterified polyol formed as in Example 36
3.0 g	Dipropylene glycol
1.0 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 67 parts A-side to 100 parts B-side at a temperature of 146° F for 1.5 minutes.

Example 39

B-side:

50.0 g	Transesterified polyol formed as in Example 36
3.0 g	Dipropylene glycol
0.5 g	Dibutyltin diacetate (T1) - catalyst

A-side: Mondur® MR light

The B-side was combined with the A-side in a ratio of 20 parts A-side to 100 parts B-side at a temperature of 141° F for 2 minutes.

Example 40

B-side:

50.0 g	Transesterified polyol formed as in Example 36
3.0 g	Dipropylene glycol
1.0 g	Dibutyltin diacetate (T1) - catalyst

A-side: Mondur® MR light

The B-side was combined with the A-side in a 1:1 ratio A-side to B-side at a temperature of 152° F and for 1 minute.

Example 41

Transesterification

350.0 g	Blown soy oil
60.0 g	Glycerin
35.0 g	White cane sugar

The above was heated at a temperature of 240°F.

Example 42

B-side:

50.0 g	Transesterified polyol formed as in Example 41 (preheated to 101° F)
3.0 g	Dipropylene glycol
1.0 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 193° F for 30 seconds.

Example 43

B-side:

50.0 g	Transesterified polyol formed as in Example 42 (preheated to 101° F)
3.0 g	Dipropylene glycol
0.8 g	Dibutyltin diacetate (T1) - catalyst

A-side: Mondur® MR light

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side and reached a temperature of 227° F for 20 seconds.

Example 44

Transesterification

35.9 g	Glycerin
6.9 g	Cane sugar
20.0 g	Trimethylolpropane (preheated to 190° F)

30 g of the above mixture was combined with 300 g of blown soy oil.

Example 45

Step 1	Heated 60 g trimethylolpropane (melting point of about 58° C, about 136.4° F) to liquid
Step 2	Heated 30 g water and added 30 g cane sugar
Step 3	Added 60 g water and cane sugar to 60 g trimethylolpropane and slowly raised the heat over 3 hours to 290° F. This drove off the water.

Example 46

B-side:

20.0 g	Transesterified polyol formed as in Example 44
0.5 g	Dibutyltin diacetate (T1) - catalyst

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 40 parts A-side to 100 parts B-side.

Example 47

Transesterification

1000 g	Glycerin
500 g	Cane sugar

The above was mixed at a temperature of 230°F for 20 minutes.

Example 48

Transesterification:

22.3 g	Reaction product formed as in Example 47
100.0 g	Blown soy oil

The above mixture was heated at a temperature of 227° F for 20 minutes.

Example 49

50 g	Water
50 g	Cane sugar

The above was mixed and heated at a temperature of 85° F for 20 minutes.

Example 50

Transesterification

20 g	Reaction mixture formed as in Example 53
100 g	Blown soy oil

The above was heated at a temperature of 185° F for 20 minutes, then heated to a temperature of 250° F for 80 minutes.

Example 51

B-side:

20.0 g	Transesterified polyol formed as in Example 50
0.4 g	Dibutyltin diacetate (T1) - catalyst

A-side: Mondur® MR light

The B-side was combined with the A-side in a ratio of 56 parts A-side to 100 parts B-side.

Example 52

B-side:

20.0 g	Transesterified polyol formed as in Example 50
0.8 g	Dibutyltin diacetate (T1) - catalyst

A-side: Mondur® MR light

The B-side was combined with the A-side in a ratio of 54 parts A-side to 100 parts B-side.

Example 53

Transesterification

3200 g	Blown soy oil (5% sugar by volume)
48 g	67% Glycerin and 37% Cane sugar mixture

Example 54

B-side:

60.0 parts by weight	Transesterified polyol formed as in Example 19
40.0 parts by weight	Polyether Polyol (Bayer® Multranol® 3901)
5.0 parts by weight	Dipropylene Glycol
2.0 parts by weight	Dibutyltin diacetate (T1) - catalyst
2.1 parts by weight	Water
109.0 parts by weight	Calcium Carbonate (filler)

A-side: Mondur® MR light

The B-side was combined with the A-side in a ratio of 56 parts A-side to 100 parts B-side.

Example 55

B-side:

50.0 g	Transesterified polyol formed as in Example 19

3.0 g	Dipropylene glycol
1.0 g	Water
0.8 g	Dibutyltin diacetate (T1) - catalyst
54.7 g	Calcium Carbonate (filler)

A-side: Bayer Corporation's Mondur® MA-2901 (Isocyanate)

The B-side was combined with the A-side in a ratio of 40 parts A-side to 100 parts B-side.

Example 56

B-side:

40.0 g	Transesterified polyol formed as in Example 53
10.0 g	Polyether polyol
1.5 g	Dipropylene glycol
1.5 g	Butanediol
1.0 g	Water
55 g	Calcium Carbonate (filler)

A-side: Modified monomeric MDI (Mondur® MA-2903)

Example 57

Transesterification

70.0 g	Trimethylolpropane
33.0 g	Pentaethertrol
60.0 g	Sugar

The above was heated to a temperature of 237° F and added 15.0 g of this reaction product to 100.0 g of blown soil oil.

Example 58

B-side:

50.0 g	Transesterified polyol formed as in Example 53
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 41 parts A-side to 100 parts B-side at a temperature of 151° F for 1 minute.

Example 59

B-side:

50.0 g	Transesterified polyol formed as in Example 53
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 177° F for 1 minute.

Example 60

B-side:

50.0 g	Transesterified polyol formed as in Example 53
3.0 g	Dipropylene glycol
3.0 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 45 parts A-side to 100 parts B-side at a temperature of 165° F for 10 seconds.

Example 61

Transesterification

200 g	Blown soy oil
20 g	Trimethylolpropane

The above was heated to a temperature of 220° F for 30 minutes.

Example 62

B-side:

50.0 g	Transesterified polyol formed as in Example 61

3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 168° F for 35 seconds.

Example 63

Transesterification:

200 g	Blown soy oil
20 g	Trimethylolpropane

The above was heated at a temperature of 325° F for 1 hour. The trimethylolpropane did not dissolve completely.

Example 64

B-side:

50.0 g	Transesterified polyol formed as in Example 63
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 151° F for 1 minute.

Example 65

Transesterification

100.0 g	Blown soy oil
5.9 g	Trimethylolpropane

The above was heated at a temperature of 235° F.

Example 66

B-side:

50.0 g	Transesterified polyol formed as in Example 65
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 162° F for 1 minute.

Example 67

B-side:

50.0 g	Transesterified polyol formed as in Example 65
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 166° F for 1 minute.

Example 68

Transesterification

2000 g	Blown soy oil
100 g	Trimethylolpropane

The above was heated at a temperature of 200° F for 2 hours.

Example 69

B-side:

50.0 g	Transesterified polyol formed as in Example 68
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The above was heated at a temperature of 166° F for 1 minute.

Example 70

B-side:

50.0 g	Transesterified polyol formed as in Example 68
4.0 g	Dipropylene Glycol
1.4 g	Dibutyltin Diacetate (T1)
1.3 g	Water

A-side: Modified monomeric MDI (Mondur® MA-2903)

Example 71

B-side:

50.0 g	Transesterified polyol formed as in Example 68
3.0 g	Dipropylene Glycol
1.0 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 61 parts A-side to 100 parts B-side at a temperature of 172°F for 1 minute.

Example 72

B-side:

50.0 g	Transesterified polyol formed as in Example 68
2.0 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The above was heated at a temperature of 135°F.

Example 73

Transesterification

200.0 g	Blown soy oil
4.0 g	Trimethylolpropane

The above was heated at a temperature of 205° F.

Example 74

B-side:

50.0 g	Transesterified polyol formed as in Example 73
2.0 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 45 parts A-side to 100 parts B-side at a temperature of 126° F.

Example 75

Transesterification

400 g	Blown soy oil
62 g	66.7% Glycerin and 33.3% cane sugar mixture

The above mixture was heated at an average temperature of 205° F.

Example 76

B-side:

40.0 g	Transesterified polyol formed as in Example 53
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.4 g	Dibutyltin Diacetate (T1)
10.0 g	Polyether Polyol (Bayer Multranol® 3901)® 3901

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 77

B-side:

40.0 g	Transesterified polyol formed as in Example 53
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.4 g	Dibutyltin Diacetate (T1)

10.0 g	Polyether Polyol (Bayer Multranol® 9151)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 78

B-side:

40.0 g	Transesterified polyol formed as in Example 75
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.4 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side.

Example 79

B-side:

20.0 g	Transesterified polyol formed as in Example 75
0.4 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side.

Example 80

B-side:

100.0 g	Transesterified polyol formed as in Example 75
2.9 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 44 parts A-side to 100 parts B-side.

Example 81

Transesterification

350 g	Blown soy oil
52 g	66.7% Glycerin and 33.3% cane sugar mixture

The above was heated at a temperature of 194° F for 4 hours.

Example 82

B-side:

40.0 g	Transesterified polyol formed as in Example 53
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.3 g	Dibutyltin Diacetate (T1)
10.0 g	Polyether Polyol (Bayer® Multranol® 3901)
97.0 g	Calcium Carbonate (filler)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 83

B-side:

20.0 g	Transesterified polyol formed as in Example 53
1.5 g	Dipropylene Glycol
1.5 g	Butanediol
0.4 g	Dibutyltin Diacetate (T1)
0.4 g	Dibutyltin Dilaurate (T12)
8.0 g	Polyether Polyol (Bayer® Multranol® 3901)

A-side: Mondur® MR Light

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 84

Transesterification

400.0 g	Blown soy oil
6.0 g	Vinegar (to add acidic proton); hydrogen chloride may also be added
60.0 g	66.7% Glycerin and 33.3% Cane sugar mixture

The above was heated at a temperature of 210° F for 1 hour.

Example 85

B-side:

40.0 g	Transesterified polyol formed as in Example 84
0.8 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side.

Example 86

B-side:

40.0 g	Transesterified polyol formed as in Example 84
0.8 g	Dibutyltin Diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 87

Transesterification

First step:

80.0 g	66.7% Glycerin and 33.3% Cane sugar
0.8 g	Vinegar

The above was heated at a temperature of 260° F for 30 minutes.

Second step:

60 g of the above reaction product was reacted with 400 g blown soy oil and mixed for 30 minutes.

Example 88

B-side:

50.0 g	Transesterified polyol formed as in Example 87
1.0 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side.

Example 89

B-side:

20.0 g	Transesterified polyol formed as in Example 87
0.5 g	Dibutyltin diacetate (T1)
20.0 g	Bayer® Multranol®

A-side: Mondur® MR Light

The B-side was combined with the A-side in a ratio of 92 parts A-side to 100 parts B-side at a temperature of 240° F for 20 seconds.

Example 90

B-side:

50.0 g	Blown soy oil
1.7 g	Dibutyltin diacetate (T1)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side.

Example 91

Transesterification

50.0 g	Blown soy oil
100.0 g	Bayer® Multranol® 9185

The above was heated to a temperature of 100° F for 5 hours.

Example 92

B-side:

50.0 g	Transesterified polyol formed as in Example 91
0.7 g	Dibutyltin diacetate (T1)

A-side: Mondur® MR Light

The B-side was combined with the A-side in a ratio of 56 parts A-side to 100 parts B-side.

Example 93

Transesterification

80.0 g	Blown soy oil
20.0 g	Polyether Polyol Bayer® Multranol® 3901

The above was heated to a temperature of 100° C.

Example 94

B-side:

50.0 g	Blown soy oil
0.8 g	Dibutyltin Dilaurate (T12)
5.0 g	Butanediol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 64 parts A-side to 100 parts B-side at a temperature of 167° F for 90 seconds.

Example 95

B-side:

50.0 g	Blown soy oil
15.0 g	Butanediol
0.8 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 131 parts A-side to 100 parts B-side at a temperature of 224° F for 20 seconds.

Example 96

2000 g	Transesterified polyol formed as in Example 80
6 g	Dipropylene glycol
6 g	Butanediol
40 g	Polyether Polyol (Bayer® Multranol® 3901)

Example 97

B-side:

50.0 g	Transesterified prepolymer polyol formed as in Example 96
0.3 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side for 120 seconds.

Example 98

B-side:

50.0 g	Transesterified prepolymer polyol formed as in Example 96
0.2 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side for 160 seconds.

Example 99

B-side:

50.0 g	Transesterified prepolymer polyol formed as in Example 96
0.4 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side for 80 seconds.

Example 100

B-side:

40.0 g	Transesterified prepolymer polyol formed as in Example 96
0.2 g	Dibutyltin Dilaurate (T12)

A-side: Mondur® MR Light mixed with 15% blown soy oil for 120 seconds.

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 101

Transesterification

400 g	Blown soy oil
60 g	66.7% Glycerin and 33% Cane sugar mixture

The above was heated at a temperature of 198° F for 5 hours.

Example 102

B-side:

50.0 g	Transesterified polyol formed as in Example 101
0.8 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 42 parts A-side to 100 parts B-side at a temperature of 149° F for 260 seconds.

Example 103

B-side:

40.0 g	Transesterified polyol formed as in Example 81
0.9 g	Dibutyltin Dilaurate (T12)
10.0 g	Bayer® Multranol®

A-side: Mondur® MR Light

The B-side was combined with the A-side in a ratio of 56 parts A-side to 100 parts B-side at a temperature of 189° F for 190 seconds.

Example 104

B-side:

40.0 g	Transesterified polyol formed as in Example 81
3.0 g	Butanediol
0.9 g	Dibutyltin Dilaurate (T12)
10.0 g	Bayer® Multranol®

A-side: Mondur® MR Light

The above was heated at a temperature of 220° F for 116 seconds.

Example 105

Transesterification

400 g	Blown soy oil
60 g	66.7% Glycerin and 33.3% Cane Sugar

Example 106

B-side:

50.0 g	Transesterified polyol formed as in Example 81
0.8 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 107

B-side:

50.0 g	Transesterified polyol formed as in Example 101
0.9 g	Dibutyltin Dilaurate (T12)

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 14 parts A-side to 100 parts B-side.

Example 108

Transesterification

200.0 g	Blown soy oil
14.3 g	Honey

The above was heated at a temperature of 200° F for 3 hours.

Example 109

B-side:

50.0 g	Transesterified polyol formed as in Example 81
0.1 g	Dibutyltin Dilaurate (T12)
10.0 g	Polyether Polyol (Bayer® Multranol® 3901)
1.5 g	Dipropylene glycol
1.5 g	Butanediol

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 110

B-side:

40.0 g	Transesterified polyol formed as in Example 81
0.2 g	Dibutyltin Dilaurate (T12)
10.0 g	Polyether Polyol (Bayer® Multranol® 3901)
1.5 g	Dipropylene glycol
1.5 g	Butanediol
0.2 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 111

B-side:

80.0 g	Transesterified polyol formed as in Example 81
20.0 g	Polyether Polyol (Bayer® Multranol® 3901)
3.0 g	Dipropylene glycol
3.0 g	Butanediol
0.4 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 112

B-side:

80.0 g	Transesterified polyol formed as in Example 81
20.0 g	Polyether Polyol (Bayer® Multranol® 3901)
3.0 g	Dipropylene glycol
3.0 g	Butanediol
0.6 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 113

B-side:

50.0 g	Transesterified polyol formed as in Example 81
0.8 g	Dibutyltin Dilaurate (T12)
10.0 g	Polyether Polyol (Bayer® Multranol® 3901)
62.0 g	Calcium Carbonate filler

A-side: Mondur® MR Light

The B-side was combined with the A-side in a ratio of 56 parts A-side to 100 parts B-side.

Example 114

B-side:

50.0 g	Transesterified polyol formed as in Example 81
0.2 g	Dibutyltin Dilaurate (T12)
0.2 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side:

20 %	Modified monomeric MDI (Mondur® MA-2903)
80 %	Mondur® MR Light

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 115

Transesterification

389.0 g	Blown soy oil
13.0 g	Dipropylene glycol
31.6 g	Polyether Polyol (Bayer® Multranol® 3901)

381.5 g	Dibutyltin Dilaurate (T12)

Example 116

B-side:

40.0 g	Transesterified polyol formed as in Example 81
10.0 g	Polyether Polyol (Bayer® Multranol® 9196)
0.4 g	Dibutyltin Dilaurate (T12)

A-side:

20.0 g	Modified monomeric MDI (Mondur® MA-2903)
80.0 g	Mondur® MR Light

The B-side was combined with the A-side in a ratio of 82 parts A-side to 100 parts B-side.

Example 117

B-side:

40.0 g	Transesterified polyol formed as in Example 101
0.1 g	Dibutyltin Dilaurate (T12)
1.5 g	Dipropylene glycol
10.0 g	Polyether Polyol (Bayer® Multranol® 3901)
0.4 g	Air Products DBU® = urethane catalyst (1,8 Diazabicyclo [5.4.0])

A-side: Modified monomeric MDI (Mondur® MA-2903)

The B-side was combined with the A-side in a ratio of 72 parts A-side to 100 parts B-side.

Example 118

B-side:

50.0 g	Transesterified polyol formed as in Example 81
0.5 g	Dibutyltin Dilaurate (T12)
2.0 g	Butanediol
20.0 g	Polyether Polyol (Bayer® Multranol® 9196)

A-side:

20 %	Modified monomeric MDI (Mondur® MA-2903)
80 %	Mondur® MR Light

The B-side was combined with the A-side in a ratio of 88 parts A-side to 100 parts B-side.

Example 119

B-side:

50.0 g	Transesterified polyol formed as in Example 81
20.0 g	Polyether Polyol (Bayer® Multranol® 9196)
0.5 g	Dibutyltin Dilaurate (T12)
2.0 g	Dipropylene Glycol

A-side:

20 g	Modified monomeric MDI (Mondur® MA-2903)
80 g	Mondur® MR Light

Example 120 (Water blown TDI seating-type foam)

B-side:	50.0 g	Transesterified blown soy oil
	50.0 g	Conventional polyol (3 Functional, 28 OH, 6000 Molecular weight, 1100 viscosity)
	0.8 g	Non-acid blocked Dibutyltin dilaurate catalyst
	0.8 g	Flexible blowing catalyst (Bis(N,N, dimethylaminoethyl)ether),
	1.0 g	Flexible foam silicon surfactant
	1.0 g	Water
A-side:	2,4-Toluene Diisocyanate (TDI)	

The B-side was combined with the A-side in a ratio of 40 parts A-side to 100 parts B-side.

Example 121 (Hydrocarbon blown TDI seating-type foam)

B-side:	50.0 g	Transesterified blown soy oil
	50.0 g	Conventional polyol (3 Functional, 28 OH, 6000 Molecular weight, 1100 viscosity)

	0.8 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.8 g	Flexible blowing catalyst (Bis(N,N,dimethylaminoethyl)ether)
	1.0 g	Flexible foam silicone surfactant
	4.0 g	Cyclopentane, or other suitable blowing agents
A-side:		2,4-Toluene Diisocyanate (TDI)

The B-side was combined with the A-side in a ratio of 40 parts A-side to 100 parts B-side.

Example 122 (Water blown MDI seating-type foam)

B-side:	100.0 g	Transesterified blown soy oil
	1.0 g	Flexible foam surfactant
	1.6 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	3.0 g	Water
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 65 parts A-side to 100 parts B-side.

Example 123 (Hydrocarbon blown MDI seating-type foam)

B-side:	100.0 g	Transesterified blown soy oil
	1.0 g	Flexible foam surfactant
	1.6 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	6.0 g	Cyclopentane, or other suitable blowing agent
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 65 parts A-side to 100 parts B-side.

Example 124 (Water blown higher rebound MDI searing-type foam)

B-side:	50.0 g	Transesterified blown soy oil
	50.0 g	Conventional polyol (3-functional, 28 OH,

		6000 molecular weight, 1100 viscosity)
	1.0 g	Flexible foam surfactant
	0.3 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.4 g	Non-acid blocked Alkyltin mercaptide catalyst
	3.0 g	Water
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 125 (Hydrocarbon blown higher rebound MDI searing-type foam)

B-side:	50.0 g	Transesterified blown soy oil
	50.0 g	Conventional polyol (3 Functional, 28 OH, 6000 Molecular weight, 1100 Viscosity)
	1.0 g	Flexible foam surfactant
	0.3 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.4 g	Non-acid blocked Alkyltin mercaptide catalyst
	6.0 g	Cyclopentane, or other suitable blowing agents
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 62 parts A-side to 100 parts B-side.

Example 126 (Water blown lightweight rigid urethane material)

B-side:	50.0 g	Transesterified blown soy oil
	1.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	1.0 g	Water
A-side:	100%	Polymeric MDI (Methylenebisdipenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 127 (Hydrocarbon blown lightweight rigid urethane material)

B-side:	100.0 g	Transesterified blown soy oil
	1.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	3.0 g	Cyclopentane, or other suitable blowing agents
A-side:	100%	Polymeric MDI (Methylenebisdipenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 128 (Dense rigid urethane material)

B-side:	100.0 g	Transesterified blown soy oil
	1.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst
A-side:	100%	Polymeric MDI (Methylenebisdipenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

Example 129 (Very dense rigid urethane material)

B-side:	100.0 g	Transesterified blown soy oil
	1.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst
A-side:	100%	Polymeric MDI (Methylenebisdipenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 110 parts A-side to 100 parts B-side.

Example 130 (Semi-flexible carpet backing material)

B-side:	80.0 g	Transesterified blown soy oil
	20.0 g	Conventional polyol (2 Functional, 28 OH, 4000 Molecular weight, 820 Viscosity)
	0.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst

	0.5 g	Non-acid blocked Alkyltin mercaptide catalyst
	4.0 g	Dipropylene glycol
A-side:	100%	Monomeric MDI (methylenebisdiphenyl diisocyanate) (23% NCO, 500 Viscosity, 183 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 45 parts A-side to 100 parts B-side.

Example 131 (Semi-flexible carpet backing material)

B-side:	80.0 g	Blown soy oil
	20.0 g	Conventional polyol (2 Functional, 28 OH, 4000 Molecular weight, 820 Viscosity)
	0.2 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.5 g	Non-acid blocked Alkyltin mercaptide catalyst
	4.0 g	Dipropylene glycol
A-side:	50%	4,4-MDI (methylenebisdiphenyl diisocyanate) Isocyanate
	50%	2,4-MDI (methylenebisdiphenyl diisocyanate)Isocyanate mixture (33.6% NCO, 10 Viscosity, 125 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 34 parts A-side to 100 parts B-side.

Example 132 (Flexible carpet padding material)

B-side:	85.0 g	Transesterified blown soy oil
	7.5 g	Conventional polyol (3 Functional, 28 OH, 4000 Molecular weight, 1100 Viscosity)
	7.5 g	Conventional polyol (4 Functional, 395 OH, 568 Molecular weight, 8800 Viscosity)
	0.1 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.2 g	Non-acid blocked Alkyltin mercaptide catalyst
	2.0 g	Dipropylene glycol
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side.

<u>Example 133</u> (Fast-set hard skin coating material)

B-side:	100.0 g	Transesterified blown soy oil
	1.0 g	Flexible foam surfactant
	0.8 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.8 g	Fast acting Amicure DBU® (Bicyclic Amidine) catalyst
A-side:	100%	Isocyanate terminated PPG (polypropylene ether glycol) Prepolymer (19% NCO, 400 Viscosity, 221 Equivalent weight, 2 Functional)

The B-side was combined with the A-side in a ratio of 68 parts A-side to 100 parts B-side.

<u>Example 134</u> (Wood molding substitute material)

B-side:	100.0 g	Transesterified blown soy oil
	2.0 g	Trimethylolpropane
	1.0 g	Non-acid blocked Dibutyltin Dilaurate catalyst
A-side:	100%	Polymeric MDI (methylenebisdiphenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 80 parts A-side to 100 parts B-side.

<u>Example 135</u> (Semi-rigid floral foam type material)

B-side:	100.0 g	Transesterified blown soy oil
	0.5 g	Non-acid blocked Dibutyltin Dilaurate catalyst
	0.5 g	Fast acting Amicure DBU (Bicyclic amidine) catalyst
	5.0 g	Water
A-side:	100%	Polymeric MDI (methylenebisdiphenyl diisocyanate) (31.9% NCO, 200 Viscosity, 132 Equivalent weight, 2.8 Functional)

The B-side was combined with the A-side in a ratio of 70 parts A-side to 100 parts B-side. A colorant (green) may be added if desired.

While vegetable oil based transesterified polyols are preferred in urethane production, an alternative embodiment of the present invention includes a cellular material that is the reaction product of an A-side and a B-side, where the A-side is comprised of an isocyanate and the B-side comprises a vegetable oil, or a blown vegetable oil, a cross-linking agent comprised of a multi-functional alcohol, and a catalyst. This alternative further comprises a method for preparing a cellular material comprising the reactive product of an A-side comprised of a prepolymer diisocyanate and a B-side. The B-side comprises a first vegetable oil, a cross-linking agent comprised of a multifunctional alcohol, a catalyst, and optionally, a blowing agent.

There are several methods of application and production available for the vegetable oil based polyurethanes of the present invention including non-transesterified vegetable oil based urethane transesterified vegetable oil based urethane, urethanes where a polyol is oxylated, and/or vegetable oil based urethanes where the vegetable oil has been neutralized prior to reacting it in the B-side with the isocyanate A-side.

The A-side and B-side materials of the present invention are typically mixed prior to application onto a substrate either via a static mixer or more typically an impingement spray applicator. A static mixer or similar premixing device may be used to mix the A-side and B-side prior to application. As seen in Figure 1, the preferred impingement spray gun applicator 10 of the type used in connection with the method of the present invention includes a handle portion 12 having a grip 14, a protecting portion 16 to protect the finger, and a trigger 18 that turns on the flow of A-side and B-side components. The spray gun applicator 10 also includes an A-side intake 20, a B-side intake 22 and a nozzle spray gun applicator head 24 that includes an A-side outlet 21 and a B-side outlet 23, which in the preferred embodiment, are combined into a single nozzle. Of course, separate external nozzles for each of the A-side outlet 21 and B-side outlet 23 can be advantageously employed. It is possible, but not typical, for a bio-based urethane material of the present invention to be applied using two impingement spray applicators with focused spray patterns directed such that the A-side and B-side reactants substantially mix prior to contacting the substrate material.

As shown in Figure 2, the present invention further includes the method of lining a boat hull 26 (either the inside or outside) of a boat 25 with a urethane material of the present

invention to create a composite. Such linings are typically for floatation, strength, sound absorption, and fire retardation where preferably incorporating fire retardant.

As shown in Figure 3, the present invention further includes the method of applying a urethane material of the present invention to a vehicle 30 or vehicle component to create a composite, typically a vehicle cargo bay 31, such as the truck bed shown. The urethane material of the present invention may be used to coat any part of a vehicle. An elastomer urethane material of the present invention, as is typical with most coatings of the present invention, is used when it is desired to protect a surface from the elements or from damage from debris of any sort - especially appropriate when the substrate to be coated with the urethane material is a vehicle cargo bed or the like. However, more cellular/foam type urethane material of the present invention can also be used according to the method of the present invention and is typically used when coating a material that requires sound damping or cushioning properties as in vehicle doors and other portions of vehicles where such properties are desired.

The typical formulation for a spray-on bedliner elastomer, which Applicants currently believe will work on other substrates as well including boat hulls and building materials includes the following:

	Ingredient	Amount (% w/w)
B-side:	about 2000 molecular weight Polyether amine polyol	about 10% - about 15%
	About 400 molecular weight Polyether amine polyol	about 2% - about 5%
	About 4800 molecular weight Polyether polyol	about 8% - about 12%
	Blown vegetable oil, Transesterified vegetable oil or other modified vegetable oil of the present invention	about 12% - about 18%
	cross-linker (when using blown or crude vegetable oil as typically utilized)	about 5% - about 8%
	surfactant (optional)	about 0.01% - about 1%

	Moisture Absorber (optional)	about 0.01% to about 2%
<u>A-side</u>:	Isocyanate	about 38% - about 45%

As shown in Figure 4, another aspect of the present invention includes applying a urethane material of the present invention to a building component to create a composite, specifically shown in Figure 4 is the coating of a building roof 33, which is typically coated with an elastomeric/rigid urethane material. Any building or structural component may have any urethane material (either elastomeric/rigid or a foam) applied to it in accordance with the present invention as needed for a given application. Wood, concrete, a metal such as steel, or asphalt may all be coated with the urethane material of the present invention. As seen in Figure 5, a cellular or elastomeric/rigid urethane material of the present invention, although more typically a cellular material, may be used to insulate or line a portion of the interior of a building structure 32 of a building 35. Of course, as appropriate, a fire retardant is preferably included in the urethane material and all local building codes and customs should be followed.

As shown in Figures 6-7, any urethane material of the present invention may be employed advantageously to coat a carpet material 50 through applicator 56 to create a composite. When the carpet material 50 is coated with a urethane material 52 of the present invention, a computer controlled X-axis and Y-axis control system operated by computer 54 is used to control the position of the applicator fixture 38 or applicator fixture 38 used to apply the urethane material relative to conveyor 36. While one impingement mix spray applicator fixture 38 is shown mounted to frame 40 (Fig. 6), two impingement mix spray applicator fixtures 38 may also be used and directed such that the A-side and B-side reactants mix prior to contacting the substrate (carpet material) surface (Fig. 7). Conceivably, the urethane material could be manually applied to the carpet backing, but there would be an increased chance that the urethane material would be of inconsistent thickness or too thin.

Using the present invention to apply a urethane material to the surface of a carpet material allows a small building to be used to apply carpet backing to a carpet's griege goods whereas, in the prior art, much larger facilities with ovens as long as about 300 feet at temperatures as high as 300°F were required to apply conventional petroleum based urethane materials as carpet backings to carpet materials. When polyurea or other similar compounds are added to the B-side of any of the bio-based urethane material of the present invention, the cure time is increased such that the carpet backing urethane material applied in accordance with the

present invention allows the carpet material to be rolled onto itself without damaging the carpeting material after only seconds. This allows for multiple X and Y axis computer controlled systems to coat the carpet material much quicker and in a smaller space.

The use of the impingement mix spray applicators has the added benefit of forcing more urethane material into the carpet backing fibers, which are essentially carpet fiber woven into or otherwise attached to a primary backing material. This produces a carpet material where the tufts have superior pull strength (the tufts are more firmly held in place) because more of the urethane material is forced into contact with the tufts and the primary backing material, a greater mechanical and chemical bond is made between the tufts and the primary backing, which holds the tufts in position.

Applicants currently believe that, to date, no one has used an impingement mix spray applicator or applicators to apply, not only a bio-based urethane material (transesterified, unmodified, blown, oxylated, or neutralized vegetable oil) as disclosed herein, but that no one has used this method to apply a conventional petroleum based urethane system to a carpet material as well. In the conventional petroleum based systems, as discussed herein, the A-side is the same as in the case of a bio-based urethane material of the present invention, but the B-side comprises conventional petroleum based polyols such as polyurea polyols, polyether polyols, and polyester polyols. The same optional agents such as blowing agents, surfactants, and the like discussed herein are also optionally used in this system.

Additionally, Applicants currently believe that Bio-based urethane materials may be produced according to the present invention and used in place of conventional petroleum based polyols in every instance, in most cases with significant cost savings and other advantages. Applicants have specifically contemplated using any of the bio-based urethane materials of the present invention for the following applications: Astroturf®, which is an artificial turf surface having an elastic underlayer shock absorbing material made with rubber or like material and a urethane binder; in injection molding; as furniture cushioning material or padding or backing material; as slab stock for mattresses and in pillows; as packaging material; in any molded foam product; as micro-cellular shoe soles, shoe liners, and shoe outers; as refrigerator cabinet insulation or insulation for various appliances in need of insulation, typically either sound or temperature insulation; as floor mats; as a coating for seeds; as an ingredient, in the cased of the bio-based polyol, in paint, as a floor coating, as a bonding and filling for natural and synthetic

wood products (these typically utilize aromatic isocyanates as an A-side reactant component), which provides better fireproofing for the wood material; and as tires for vehicles or machines.

The above description is considered that of the preferred embodiments only. Modifications of the invention will occur to those skilled in the art and to those who make or use the invention. Therefore, it is understood that the embodiments shown in the drawings and described above are merely for illustrative purposes and not intended to limit the scope of the invention, which is defined by the following claims as interpreted according to the principles of patent law, including the doctrine of equivalents.